# Carbon Nanotube-Coated Macroporous Poly(*N*-isopropylacrylamide) Hydrogel and Its Electrosensitivity

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S *Supporting Information*

ABSTRACT: A facile method of fabricating novel CNT-coated macroporous PNIPAAm hydrogel composite was proposed. The method was based on the deposition of a dense and compact CNT layer on the pore walls of the preformed macroporous PNIPAAm hydrogel scaffold. The resulted hydrogel composite exhibited an electric current sensitivity resulting from electro-thermal conversion. When an external electric current was applied, this hydrogel composite could be electrically heated and then showed a thermally induced shrink.
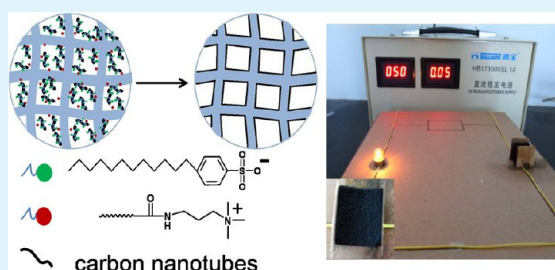
KEYWORDS: *Macroporous, CNTs, composite, electro-thermal conversion, sensitivity, switch*

Hydrogels are three-dimensional networks of hydrophilic polymers, cross-linked either through permanent covalent bonds or reversible physical cross-links. Some of the hydrogels, which are termed "intelligent" or "smart" hydrogels, can undergo a reversible volume phase transitions or gel−sol phase transitions upon small changes of the environmental conditions. These smart hydrogels have attracted the attention of the polymer society because of a large variety of applications in artificial muscles, chemical valves, enzymes immobilization, bioseparation, and so on. Stimuli applied to induce various responses of the smart hydrogel systems can be temperature, pH, light, sound, electric fields, magnetic fields, etc.[1,2]

Among the methods, electric stimulus shows especial advantages because it is clean and controllable when coupling to microelectronics in a feedback-controlled system. Up until now, electric-sensitive hydrogels have usually been made of polyelectrolytes.[3,4] They undergo shrinking or swelling in the presence of an electric field. In some cases, hydrogels show swelling on one side and deswelling on another side, resulting in bending of the hydrogels. In general, the polyelectrolyte hydrogels are ion-conductive, and the electroresponsive behavior is dramatically affected by the concentration and distribution of the ions in the system.

Electrothermal conversion is another strategy to achieve the electric sensitivity of hydrogels. When electric conductive nanoparticles, such as carbon nanotubes (CNTs), are introduced to a thermal sensitive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel matrix, the nanocomposite would be conductive. Upon application of an electric current, the electrothermal conversion takes place to raise the local temperature of the composite beyond the lower critical solution temperature (LCST, around 32 °C) of PNIPAAm. As a result, the PNIPAAm nanocomposite is capable to show an electric sensitivity. It is an indirect and contact-type electric

sensitivity, compared with the polyeletrolyte hydrogels which can be triggered directly by electric field and are always required to be placed between two electrodes in a noncontact status. In case the electric field was complicated to find and hard to apply for an electric-sensitive hydrogel system, the contact-type of electric-sensitive hydrogels would be a promising material with much more broad application.

From another perspective, it is an effective supplement to utilize the thermoresponsive PNIPAAm hydrogels which is usually directly heated by increasing the environment temperature by application of a heater or addition of hot gas or liquid, because the directly heating methods may not be preferred in some cases.[5] For example, increasing the environmental temperature may cause harm when applied in an organism. In addition, environment heating for PNIPAAm-integrated devices would become invalid in a nonheat conducting environment or in a very cold surrounding such as space or deep-sea. In these cases, indirect electric heating of an appropriately designed PNIPAAm nanocomposite would be an alternate. Furthermore, the combination of nanoparticles within gels can significantly improve the physicochemical properties of the resulting systems like optical property, thermal conductivity, mechanical strength, and so forth.[6,7]

Up until now, most of the researchers utilize in situ polymerization method to introduce CNTs into the hydrogel matrices.[8,9] In the as-fabricated hydrogel composites, CNTs are enwrapped by the hydrogel matrix. In this case, the applied external electric signals can hardly transmit through the insulated CNTs within the nonconductive hydrogel matrix unless extraordinary large content of CNTs are used or an

excellent dispersion of CNTs is achieved to form a 3D CNT network throughout the whole gel matrix. Therefore, the electrical conductivity of the composites is usually very small, thus the generated heat is insufficient to induce the thermal transition of the composites. As far as we know, the only reported success was a graphene−polymer hydrogel fabricated by an in situ hydrothermal method.[10]

In this communication, we propose a facile method for the fabrication of macroporous PNIPAAm/CNT composite hydrogel that shows a volume transition in response to a contact electrostimulus. This method is based on the electrostatic force-mediated deposition of CNTs onto the inner surface of the preformed macroporous PNIPAAm hydrogel. The pore walls of the PNIPAAm hydrogel were coated with a compact layer of interconnected CNTs. Because of the good electrical conductivity of the CNT network, electrical energy applied on the nanocomposite efficiently converted to heat and thus triggered the shape-changing capability of the material. When local temperature reached beyond the LCST of PNIPAAm because of the electrothermal conversion, the composite hydrogel showed a shrinking behavior.

The macroporous PNIPAAm hydrogel matrix was prepared by a modified cryopolymerization method based on heterogeneous initiation.[11] The resulted hydrogel using this method possesses larger interconnected pores in the swollen state and a much more rapid thermosensitivity than that fabricated by conventional cryopolymerization. Briefly, N-isopropylacrylamide (NIPAAm), N,N'-methylenebisacrylamide (BIS), (3-Acrylamidopropyl)trimethylammonium Chloride (AAPTAC) and dodecyl dimethyl benzyl ammonium bromide (DDBAB) were dissolved in deionized water at room temperature. The solution was first cooled to 0 °C followed by adding ammonium persulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TEMED), and the polymerization was carried out −8 °C for 12 h. After the reaction, the samples were immersed in excessive deionized water to remove the unreacted monomers. The resulted hydrogel sample was labeled as PNIPAAm-TAC gel. PNIPAAm gel was prepared using the same method in the absence of AAPTAC comonomer.

Figure 1 shows the process of CNT deposition onto the pore walls of the macroporous PNIPAAm hydrogel. The as-
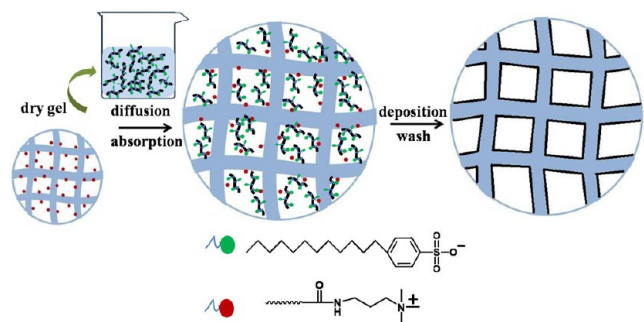

Figure 1. Process of deposition of CNTs onto the pore walls of macroporous PNIPAAm hydrogel.

fabricated PNIPAAm-TAC gel and PNIPAAm gel were freeze-dried and afterward immersed in CNT dispersions (0.1 wt %, see the details in the Supporting Information) prepared beforehand. After 30 min under slow magnetic stir, the hydrogel composites were transferred into deionized water and slightly squeezed several times to remove the free CNTs within

the pore. The obtained hydrogel composites were labeled as PNIPAAm-TAC-*dep*-CNTs and PNIPAAm-*dep*-CNTs, respectively. As shown in Figure 2, the pore size of the as-fabricated PNIPAAm-TAC and PNIPAAm gel ranged from 50 to 100 μm, which was much larger than the length of the CNTs, which is approximately 1.2 μm (see Figure S1 in the Supporting Information). So CNTs were allowed to diffuse into the inner surface of the hydrogel matrix freely. Figure 2a2, a3, b2, and b3 shows the inner-surface morphology of the PNIPAAm-*dep*-CNT and PNIPAAm-TAC-*dep*-CNT hydrogel composites. As shown in Figure 2a3, the amount of the absorbed CNTs on the pore walls of PNIPAAm-*dep*-CNT gel was small, and the CNTs deposited into several fragmentary CNT domains. A large part of the pore walls was not covered with CNTs. On the contrary, the inner surface of the PNIPAAm-TAC-*dep*-CNT gel was coated with a dense and compact CNT layer, as shown in Figure 2b3). The CNTs were interconnected with each other, forming a 3D network. So it can be concluded that the cationic comonomer AAPTAC played a critical role in enhancing the adhesion between the CNTs and the matrix. For the PNIPAAm-*dep*-CNT sample, the interaction between the CNTs and the PNIPAAm matrix was mainly van der Waals force, which was very weak so that only a small amount of the CNTs could attach onto the pore walls. In comparison, the incorporation of AAPTAC made the matrix positively charged. So there was an electrostatic force, which is much stronger than the van der Waals force, between the negatively charged CNTs and the PNIPAAm-TAC matrix. As a result, a much larger number of CNTs were able to attach and deposit on the pore walls of PNIPAAm-TAC-*dep*-CNTs than on those of PNIPAAm-*dep*-CNTs. Through thermogravimetric analysis (see Figure S2 in the Supporting Information), it was found that PNIPAAm-TAC-*dep*-CNT composite contained approximately 4.2 wt % CNTs, whereas PNIPAAm-*dep*-CNTs contained only 0.5 wt % CNTs. The molar ratio of AAPTC to NIPAAm was fixed at 3% for PNIPAAm-TAC gel. A larger amount of AATAC would dramatically increase the LCST of PNIPAAm-TAC gel (see Figure S5 in the Supporting Information), whereas the amount of deposited CNTs did not increase obviously. The Young's moduli of PNIPAAm-TAC-*dep*-CNT composite and PNIPAAm-TAC gel were 3.2 KPa and 2.5 KPa, respectively, according to the uniaxial compression test (see Figure S4 in the Supporting Information). Deposition of CNTs onto the walls of the macroporous PNIPAAm scaffold did not enhance the mechanical strength obviously because, in this case, the CNT network was not incorporated into the PNIPAAm microstructure.

The PNIPAAm-TAC-*dep*-CNT composite possessed a good electrical conductivity of 5.2×10^{-2} S/m (measured with two-probe method discussed elsewhere[10]) in the swollen state because of the interconnected CNT coating formed on the inner surface of the hydrogel matrix. This property would be attractive for potential applications. Here we studied the electric heating and the accompanying volume shrinkage of the hydrogel composite. Two platinum electrodes were fixed on a hydrogel monolith (10 mm × 10 mm × 10 mm). Different constant voltages were applied on the samples through a potentiostat. A tiny thermocouple was inserted into the core of the hydrogel to detect the temperature. Figure 3a shows the schematic setup of this experiment. Upon application of a certain voltage on the hydrogel, an electric circuit was initiated. The electrical energy converted to heat within the CNT
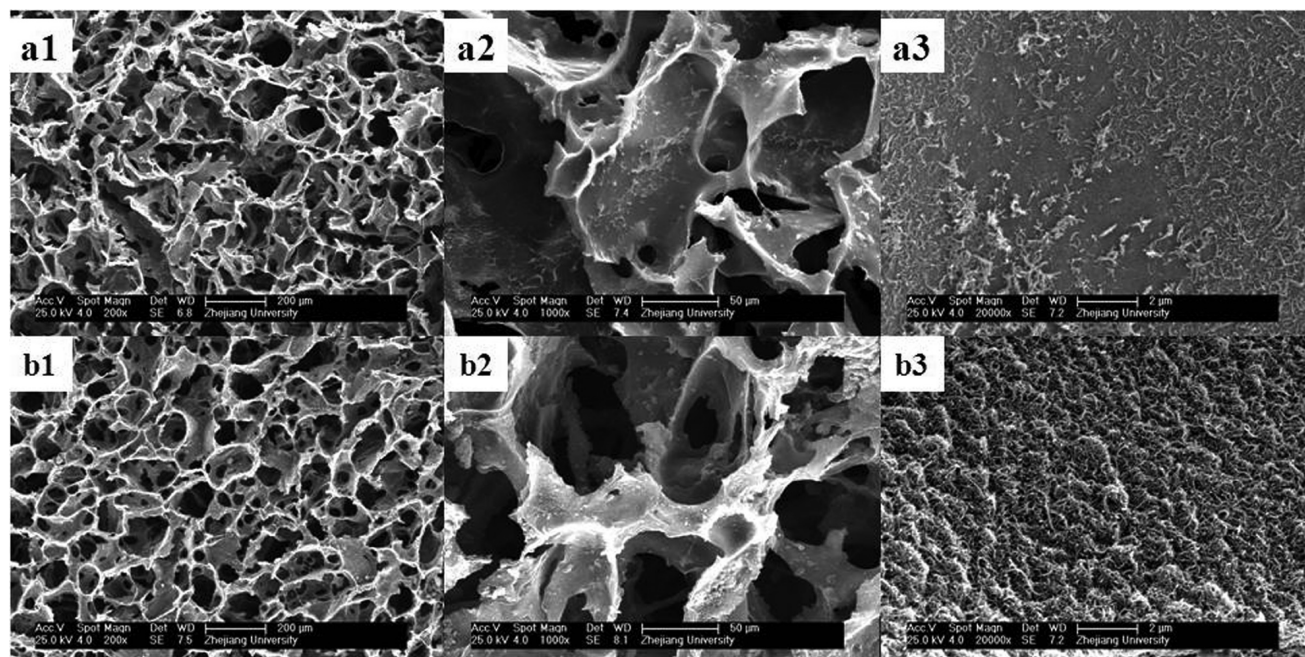
Figure 2. Cross-sectional morphology and CNT arrangement of two kinds of CNT composite hydrogel. (a1, a2, and a3) PNIPAAm-*dep*-CNTs. (b1, b2, and b3) PNIPAAm-TAC-*dep*-CNTs.
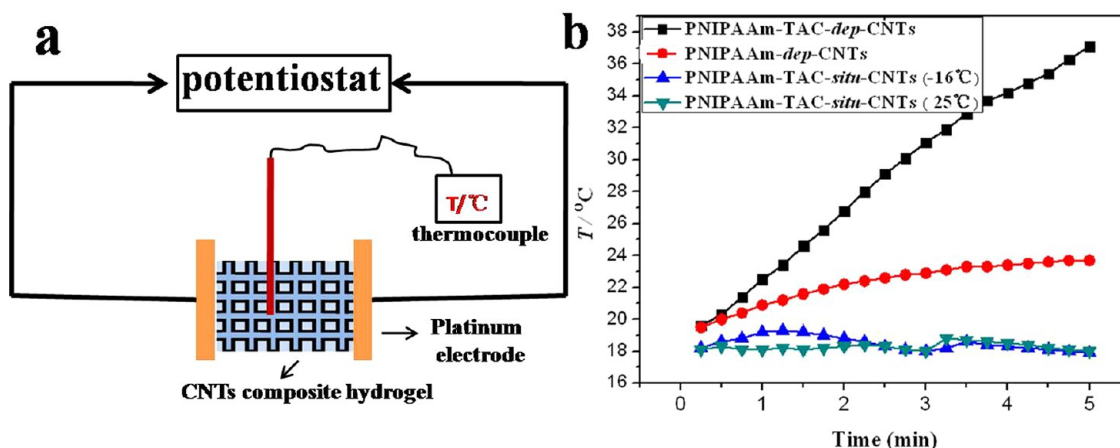

Figure 3. (a) Setup for the measurement of the temperature change of CNT composite hydrogel. (b) Temperature increase of different kinds of CNT composite hydrogels under the same applied voltage of 30 V.

network, and the heat energy further conduct to the PNIPAAm-based hydrogel scaffold. Figure 3b shows the temperature change of different CNT/hydrogel composites under a constant voltage of 30 V. PNIPAAm-TAC-*dep*-CNT gel sample underwent the fastest temperature increase. It reached 32 °C from the initial 20 °C within 4 min, and crept up to 38 °C in 5 min. PNIPAAm-*dep*-CNT gel sample showed a much slower temperature increase, rising only 3° after 5 min. This difference in the electric heating rate is derived from the different CNT deposition on the pore walls of the hydrogel matrix. PNIPAAm-TAC-*dep*-CNT gel absorbed more CNTs, which formed a more compact and denser CNT layer on the walls. This interconnected CNT network resulted in a higher electrical conductivity which was able to generate a large heat conversion. For the PNIPAAm-*dep*-CNT gel, the amount of the deposited CNTs was much smaller than that of PNIPAAm-TAC-*dep*-CNT gel. The low electrical conductivity (1.7×10^{-3} S/m) of PNIPAAm-*dep*-CNT gel resulted in a low heat

conversion within the gel. Here we also prepared two kinds of conventional PNIPAAm-TAC/CNT composite hydrogel by in situ polymerization with a similar CNT content (1.0 wt % to the NIPAAm) as contrasts. One was fabricated at room temperature and the other at −16 °C (cryogelation). They both showed no obvious temperature increase when applied on an electric current, as shown in Figure 3b. This was because in the process of in situ polymerization, individual CNTs or CNT clusters were enwrapped by the PNIPAAm chains, and they were disconnected with each other when finally embedded in the hydrogel matrix. It was hard for the electric current to "jump" from one CNT to another across the PNIPAAm-TAC matrix. So the electric circuit was not strong enough to heat the CNTs. The electrical conductivity of the both two conventional PNIPAAm-TAC/CNT composite hydrogels was too low to be detected.

When the PNIPAAm-TAC-*dep*-CNT gel was electrically heated to its LCST of 36 °C (see the Supporting Information,
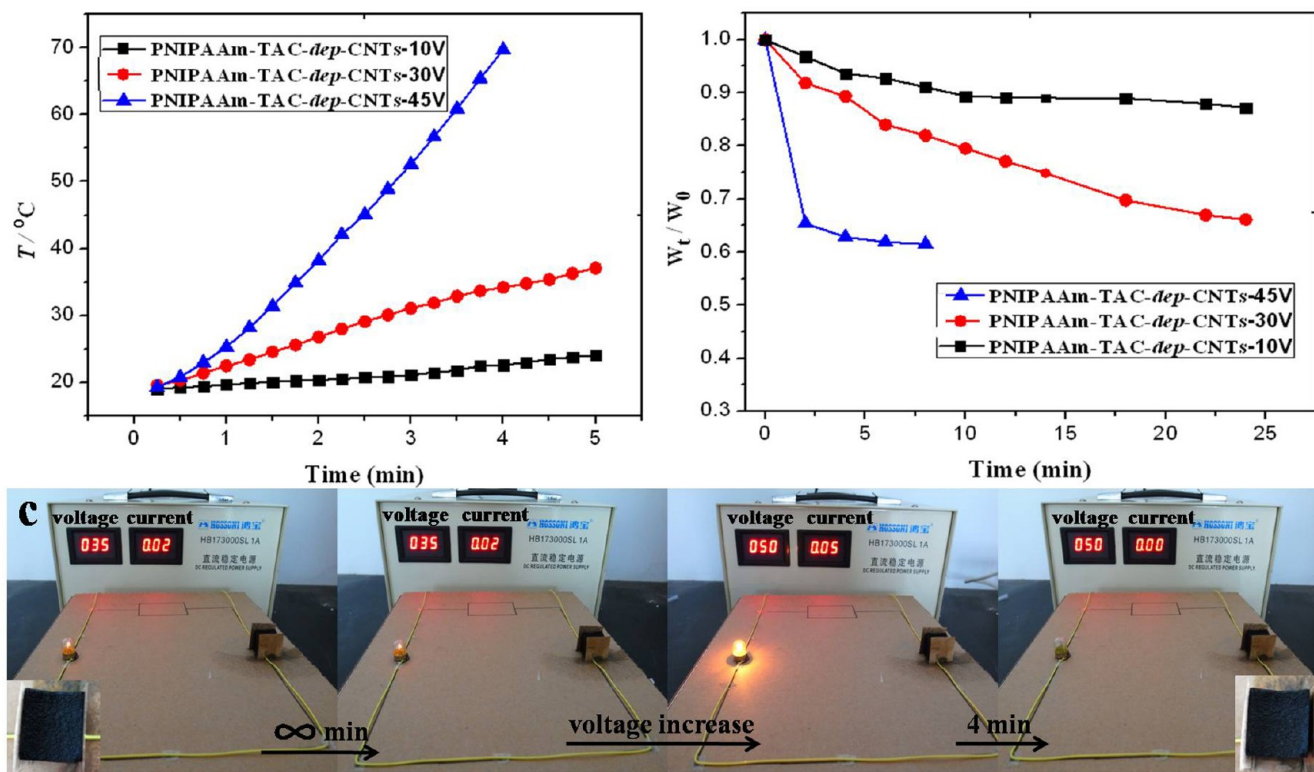
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Figure 4. (a) Temperature increase in PNIPAAm-TAC-*dep*-CNT gel under different applied voltages. (b) Shrinking kinetics of PNIPAAm-TAC-*dep*-CNT gel under different applied voltages. (c) Practical application of an on−off switch using PNIPAAm-TAC-*dep*-CNT gel.

Figure S1), it underwent a phase transition-induced weight loss and volume change. The magnitude of the external electric voltage is an important parameter to control the electric heating rate. A larger electric voltage will result in a faster heating rate because of the lager heat conversion. As shown in Figure 4a, when a 45 V voltage was applied, the sample was rapidly heated to 36 °C in about 100 s and continuously to 70 °C within 4 min. When the voltage was 30 V, it cost 5 min to heat the sample to 36 °C. In the case of application of a 10 V voltage, the temperature rose extremely slowly and was not able to reach 36 °C even after 30 min because the slowly generated heat transported to the environment (18 °C) at once rather than raising the local temperature of the composite. Figure 4b shows the shrinking kinetics of the PNIPAAm-TAC-*dep*-CNT gel in response to different applied voltages. When the applied voltage was 45 V, the gel rapidly shrunk to nearly 60% of its original weight in less than 180 s. In the case of 10 V, the shrinkage-induced weight loss was not obvious even after 25 min. This phenomenon coincided with the trends of temperature increase of the gel sample under different voltages in Figure 4a. Because the PNIPAAm-based hydrogel scaffold used here was supermacroporous in the swollen state, it would reach the shrinkage equilibrium immediately after upon temperature increase.[12] As a result, the electric-response volume-change rate of the gel was controlled by the electric heating rate. This property offers great potential application as a self-controlled on−off switch when coupling to sensors or other micro-electronics in feedback controlled systems. Figure 4c shows a practical application using PNIPAAm-TAC-*dep*-CNT gel as a switch when integrated into a circuit. When the applied voltage was low, the circuit stayed closed and the device could work normally. For a larger voltage, however, the gel shrunk and the circuit was cut off in 4 min. The inset of Figure 4c shows the

volume change of the PNIPAAm-TAC-*dep*-CNT gel. When the applied voltage was shifted to 50 V, the gel shrunk and became noncontact with the electrodes. So the PNIPAAm-TAC-*dep*-CNT gel functioned as an overcurrent protection here.

In conclusion, we propose a method of fabricating novel CNT-coated macroporous PNIPAAm hydrogel composite exhibiting an electric sensitivity. The method is based on the electrostatic force-mediated deposition of a dense and compact CNT layer on the pore walls of the macroporous PNIPAAm hydrogel scaffold. When an external electric current is applied, this hydrogel composite can be electrically heated and then shows a thermally induced shrink. This electric-sensitive hydrogel shows advantage in potential application such as on−off switch and sensors.

■ ASSOCIATED CONTENT

S **Supporting Information**

Detailed experimental procedure for preparing the macroporous PNIPAAm hydrogel, PNIPAAm/CNT composite, mechanical strength and swelling characteristics of the hydrogel composite. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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